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(54) Rapidly, Physically Drying Binder Mixtures and Their Use for Coating Wood Substrates

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RAPIDLY, PHYSICALLY DRYING BINDER MIXTURES AND THEIR USE FOR COATING WOOD SUBSTRATES

ABSTRACT OF THE DISCLOSURE

A binder composition for the production of rapidly physically drying lacquer coatings containing a) a polyisocyanate component having an NCO content of 10 to 30 wt.% and b) a hydroxy-functional polyacrylate component containing one or more hydroxy-functional polyacrylate resins having a molecular weight M_n of greater than 10,000 and a viscosity as a 40 wt.% solution in n-butyl acetate of at least 2,000 mPa.s at 23°C, in quantities corresponding to an NCO/OH equivalent ratio of 0.5:1 to 2:1, and the use of the binder mixture as the binder in solvent-containing, two-component polyurethane coating compositions for coating wood or derived timber products.

RAPIDLY, PHYSICALLY DRYING BINDER MIXTURES AND THEIR USE FOR COATING WOOD SUBSTRATES

BACKGROUND OF THE INVENTION

Field of the Invention

The invention relates to a novel binder composition suitable for the production of rapidly physically drying coatings based on a polyisocyanate component and a special, hydroxy-functional polyacrylate component, and to the use of the binder composition as a binder in rapidly physically drying coating compositions for wood and derived timber products.

Description of the Prior Art

Two-component polyurethane coating compositions based on lacquer polyisocyanates and hydroxy-functional polyacrylate resins are known. For example, DE-OS 2,460,329 describes polyacrylates which may be crosslinked with polyisocyanates. These low molecular weight products have a defined, number average molecular weight (M_n) of 500 to 2,000 and polydispersity of 0.5 to 1.5. A major disadvantage of these compositions is their physical drying behavior, which is inadequate for industrial applications. Rapid physical drying, i.e., the rapid production of a tack-free coating long before complete chemical crosslinking is a fundamental requirement for the suitability of the coating compositions in large scale industrial lacquer coatings, particularly for wood and derived timber products.

In contrast to the above coatings, the two-component polyurethane coatings based on hydroxy-functional polyacrylate resins described in EP-A 0,068,383 do exhibit distinctly improved drying behavior, but still do not fulfil the stringent requirements in this regard, particularly for industrial wood and furniture coatings.

Due to these problems, in commercial applications rapidly physically drying binders such as cellulose acetate butyrate (CAB) or

nitrocellulose (NC) are always added to wood and furniture coatings based on organic polyisocyanates and known polyacrylate resins to achieve the required drying speeds. Apart from the use of an additional binder component, frequently observed disadvantages of such coating compositions are excessive yellowing of the lacquer coating (NC) or poor compatibility with the polyisocyanate component, particularly with aromatic polyisocyanates (CAB).

An object of the present invention is to provide a two-component binder compositions based on organic polyisocyanates and hydroxy-functional polyacrylate resins, which do not have the stated disadvantages of the prior art, i.e. they are suitable for the production of rapidly physically drying coatings without the addition of the rapidly physically drying binders such as NC and/or CAB.

This object may be achieved with the binder compositions according to the invention which are described in greater detail below.

SUMMARY OF THE INVENTION

The present invention relates to a binder composition for the production of rapidly physically drying coating compositions containing

a) a polyisocyanate component having an NCO content of 10 to 30 wt.% and containing one or more organic polyisocyanates and

b) a hydroxy-functional polyacrylate component containing one or more hydroxy-functional polyacrylate resins having a number average molecular weight (M_n) of at least 10,000 and a viscosity as a 40 wt.% solution in n-butyl acetate at 23°C of at least 2,000 mPa.s,

wherein components a) and b) are present in amounts sufficient to provide an NCO/OH equivalent ratio of 0.5:1 to 2.0:1.

The present invention also relates to the a solvent-containing, two-component polyurethane coating composition containing this binder

mixture as the binder, in particular for coating wood or derived timber products.

DETAILED DESCRIPTION OF THE INVENTION

Binder component a) according to the invention is selected from known lacquer polyisocyanates, i.e., in particular, polyisocyanates having biuret, urethane or isocyanurate groups and an average NCO functionality of more than 2, preferably 2.5 to 6. These polyisocyanates may have aromatically, cycloaliphatically or aliphatically bound isocyanate groups. Polyisocyanates with aliphatically and/or cycloaliphatically bound isocyanate groups are preferred for lightfast coatings.

The lacquer polyisocyanates to be used according to the invention are produced in known manner by the reaction of monomeric organic diisocyanates to form polyisocyanates containing biuret, urethane or isocyanurate groups. After their preparation, any excess monomeric starting isocyanate is removed, preferably by distillation, such that a maximum of 0.7 wt.%, preferably a maximum of 0.5 wt.%, of excess diisocyanate is present in the lacquer polyisocyanates according to the invention. The lacquer polyisocyanates generally have an NCO content, based on solids, of 10 to 30 wt.%, preferably 15 to 25 wt.%.

Suitable diisocyanates for the production of the lacquer diisocyanates include 2,4- and/or 2,6-diisocyanatotoluene, 2,4'-diisocyanatodicyclohexylmethane, 4,4'-diisocyanatodicyclohexylmethane, hexamethylene diisocyanate and 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI). Particularly preferred lacquer polyisocyanates include polyisocyanates which contain biuret groups and are prepared from hexamethylene diisocyanate, for example, those according to U.S. patent 3,124,605; polyisocyanates which contain urethane groups and are prepared from 2,4-diisocyanatotoluene, trimethyolpropane and optionally low molecular weight alkane diols, for example those according

to U.S. patent 3,183,112; polyisocyanates which contain isocyanurate groups and are prepared from 2,4-diisocyanatotoluene, hexamethylene diisocyanate, IPDI, mixtures of 2,4-diisocyanatotoluene with hexamethylene diisocyanate or mixtures of hexamethylene diisocyanate with IPDI.

At a solids content of 50 wt.%, the hydroxy-functional polyacrylate resins b) have solution viscosities which are no longer measurable using the method described below. Any further viscosity values stated below thus relate to 40 wt.% solutions in n-butyl acetate measured at 23°C.

The solution viscosities of the polyacrylates to be used according to the invention, measured as 40% solutions in n-butyl acetate at 23°C in a rotational viscometer, are at least 2,000 mPa.s, preferably 2,000 to 30,000 mPa.s and more preferably 2,000 to 25,000 mPa.s. The polyacrylate stated in EP 0 068 383 (example 1) has a viscosity of 530 mPa.s under identical conditions (solvent, solids content, temperature).

The polyacrylate resins b) generally have a number average molecular weight (M_n, determined by gel permeation chromatography) of at least 10,000, preferably 10,000 to 120,000 and more preferably 10,000 to 100,000. These and all subsequent molecular weights of component b) are determined by the molecular weight determination method described by Z. Grabisic, P. Rempp and H. Benoit in J. Polymer Sc., part B, Polym. Lett. 5 (1967), p. 753, i.e., using gel permeation chromatography.

The disclosure in US-Patent 4 442 145 (EP 0 068 383) with respect to the molecular weight of the polyhydroxy polyacrylates seems to be erroneous because a repetition of example 1 of said patent leads to a polyacrylate resin having molecular weights determined in accordance with the above method which are clearly lower than 47.700 (Mw = 24.000 resp. Mn = 6.100). In analogy thereto the repetition of example 2 of said patent leads to a polyacrylate resin having a molecular weight Mw of 27.100 and Mn of 5.200.

The monomers used to prepare copolymers b) are selected from 2.5 to 30, preferably 2.5 to 20 wt.%, of monomers A), 30 to 90, preferably 55 to 80 wt.% of monomer B), 0 to 50, preferably 0 to 30 wt.% of monomer C), 0 to 2 wt.% of monomers D) and 0 to 50, preferably 0 to 30 wt.% of monomers E).

Monomers A) are selected from monomers containing hydroxyl

groups, in particular hydroxyalkyl esters of α,ß-unsaturated carboxylic acids, preferably acrylic acid or methacrylic acid with 2 to 12, preferably 2 to 6 carbon atoms in the hydroxyalkyl residue. Examples include 2-hydroxyethyl acrylate, the isomeric hydroxypropyl acrylates (in particular, those obtained by the addition of propylene oxide onto acrylic acid), the isomeric hydroxybutyl acrylates, the isomeric hydroxypentyl acrylates, the isomeric hydroxyhexyl acrylates, the methacrylates corresponding to these acrylates and mixtures of any of these acrylates and/or meth-acrylates. Preferred monomers A) are 2-hydroxyethyl (meth)acrylates and/or the isomeric hydroxypropyl (meth)acrylates.

As may be seen from the examples of suitable (meth)acrylates, the hydroxyalkyl esters containing hydroxyl groups may have both primary and secondary hydroxyl groups. Monomers A) are used in amounts, within the above-stated ranges, that the resulting acrylate resins have a hydroxyl group content of 0.5 to 5, preferably 1 to 3 wt.%, based on solid resin.

Methyl methacrylate is used as monomer B). Styrene is used as optional monomer C). Optional monomer D) is selected from free acids, such as itaconic acid, crotonic acid, semiesters of maleic or fumaric acid, and preferably acrylic acid or methacrylic acid.

Optional monomers E) are selected from any desired olefinically unsaturated monomers, other than those used as monomers A) to D). Examples of suitable monomers include (meth)acrylic acid alkyl esters and/or cycloalkyl esters with 1 to 18, preferably 1 to 8 carbon atoms, in the alkyl or cycloalkyl residue, such as the methyl, ethyl, n-propyl, n-butyl, isopropyl, isobutyl, t-butyl, the isomeric pentyl, hexyl, octyl, dodecyl, hexadecyl, octadecyl, 3,5,5-trimethylcyclohexyl, isobornyl and/or cyclohexyl esters of these acids, with the exception of methyl methacrylate. Additional suitable monomers include acrylonitrile, vinyl

ethyl ether, methacrylonitrile, vinyl acetate, vinyl chloride, vinyl toluene, anhydride-functional, unsaturated monomers such as itaconic anhydride or maleic anhydride and any desired mixtures of the preceding monomers.

The copolymerization reaction is preferably conducted in an organic solution, optionally in the presence of inert solvents. Examples include toluene, xylene, chlorobenzene, n-butyl acetate, ethyl acetate, ethylene glycol acetate, the isomeric pentyl acetates, hexyl acetates, methoxypropyl acetate, tetrahydrofuran, dioxane, acetone, methyl ethyl ketone, higher substituted aromatics (such as solvent naphtha, crude benzene, Solvesso solvents, Shellsol solvents), higher-boiling aliphatic and cycloaliphatic hydrocarbons (such as gasoline, mineral spirits, Isopar solvents, Nappar solvents, tetralin and decalin) and mixtures of these solvents.

n-Butyl acetate, methoxypropyl acetate, xylene and mixtures of these solvents are the preferably used as solvents. In the copolymerization reaction, the solvents are generally used in quantities of 50 to 70 wt.%, based on the total weight of the reaction mixture.

The viscosity of polyacrylate resins b), which is essential to the invention, is achieved not only by the above-stated selection of suitable monomers, but also by a suitable combination of polymerization temperature with the type and quantity of initiator.

In general, the polymerization is conducted at a temperature of 80 to 150°C, preferably 90 to 120°C and more preferably 100 and 115°C.

Suitable initiators are those with a half-life of between 5 minutes and 2 hours at the stated temperature range. Examples include dilauroyl peroxide, tert.-butyl peroxy-2-ethylhexanoate, tert.-butyl peroxydiethylacetate, dibenzoyl peroxide, tert.-butyl peroxyisobutyrate, 1,1-di-tert.-butylperoxy-3,3,5-trimethylcyclohexane, 1,1-di-tert.-butylperoxycyclo-

hexane, tert.-butyl peroxy-3,3,5-trimethylhexanoate, tert.-butyl peroxy-isopropylcarbonate, 2,2-di-tert.-butylperoxybutane and tert.-butyl peroxy-stearyl-carbonate.

The initiators are generally used in an amount of 0.5 to 5, preferably 1 to 3 wt.%, based on the weight of monomers A) to E). This amount is based on solvent-free initiators and solvent-free monomers.

Polyacrylate resins b) are most preferably produced using n-butyl acetate as the solvent and tert.-butyl peroxy-2-ethylhexanoate as the initiator at temperatures of 100-115°C.

The binder mixtures according to the invention are produced by blending components a) and b), preferably with the addition of the preceding solvents, such that 30 to 50 wt.% solutions of the stated binder components are produced. The amounts are also selected such that an NCO/OH equivalent ratio of 0.5:1 to 2:1, preferably 0.5:1 to 1.5:1 is obtained.

The binder mixtures according to the invention are used for coating any desired substrates, preferably for coating wood or derived timber products and more preferably for coating furniture.

Apart from the binder mixtures according to the invention, the coating compositions may also contain known additives. Examples include flow-control agents such as oligoalkyl acrylates; pigments and extenders; viscosity-controlling additives such as bentonites and silicic acid esters; flatting agents such as silica, aluminum silicates and high molecular weight waxes; and catalysts for the isocyanate addition reaction such as for example tin(II) octoate or dimethylbenzylamine.

The coating compositions containing the binder mixtures according to the invention may be applied to the substrate to be coated using any known methods such as spraying, brushing, dipping, pouring or rolling. Wood and derived timber products (furniture) are particularly preferred

substrates.

The coatings produced with the coating compositions according to the invention are generally tack-free within a period of 30 to 70 minutes at 23°C (physical drying).

The following examples are intended to illustrate the subject matter of the invention in greater detail. All parts and percentages are by weight, unless otherwise indicated.

EXAMPLES

Production of polyhydroxyacrylates b)

The solvent (n-butyl acetate in parts by weight) was introduced into a glass flask and heated to 110°C. The monomer mixtures (parts by weight) set forth in Table I were then added over a period of 2 hours. The initiator solution was added incrementally over a period of 3 hours in parallel with the addition of the monomers. The reaction mixture was then stirred for a further 2 hours at 100°C. Viscosities and properties of the products are set forth in Table II.

Table I

Examples	1	2	3	4	5
Butyl acetate	1961	1961	1920	1920	1920
Monomer Composition					
Methyl methacrylate	1195	1002.6	1009.5	1214.8	1012.6
2-Ethylhexyl acrylate	-	203.4	205.7	—	—
Styrene	-	—	—	—	190
Hydroxyethyl methacrylate	227.7	231.4	232.4	232.8	233.2
Acrylic acid	29.0	14.3	14.4	14.4	18.2
Initiator Solution					
tert.-Butyl peroxy-2-ethylhexanoate	34.9	34.9	20.0	20.0	28.0
Butyl acetate	152.4	152.4	198.0	198.0	198.0
	3600.0	3600.0	3600.0	3600.0	3600.0

Table II compares the properties of the products of Examples 1-5 with the properties of those from Examples 1 and 2 of EP-A-0 068 383 (examples 6 and 7 in Table II).

Table II

						Comparison Examples	
Examples	1	2	3	4	5	6	7
Solids content (%)*	40.5	40.0	39.7	41.0	40.2	40.0	40.0
Viscosity (mPa·s) at 23°C**	3740	2210	7820	33390	23150	530	890

* Solids (non-volatiles) content was determined to according to DIN 53 216.

** Viscosity was determined in a Contraves rotational viscosimeter. All products were dissolved in butyl acetate. Measurements were made according to DIN 53 019, part I. (Measurement of viscosities and flow curves with standard geometry rotational viscosimeters).

Comparison of the viscosities demonstrates the clear difference between the polyacrylate resins according to the invention and those according to EP-A 0,068,383.

There are also clear differences in molecular weight, as is apparent from the following comparison between Examples 1 and 2 (according to the invention) and Examples 6 and 7 (comparison examples). The molecular weight set forth in Table III was determined using method set forth above. It may readily be seen that the molecular weights of the polyacrylate resins according to the invention were distinctly higher than those of the polyacrylate resins according to EP-A-0,068,383.

Table III

	M_w	M_n	Polydispersity
Polyacrylate from Example 1	65100	26800	1.4
Polyacrylate from Example 2	58600	22500	1.6
Polyacrylate from Example 6*	24000	6100	2.9
Polyacrylate from Example 7*	27100	5200	4.2

* Comparison example

Practical examples

Several lacquers were prepared using the polyacrylates set forth in Table IV. The polyacrylates were diluted with butyl acetate such that after the addition of the cross-linking agent solution, a spray viscosity of 18 seconds (23°C) in a DIN 4 cup was obtained. The cross-linking agent solution was a 75% solution in methoxypropyl acetate/xylene (1:1) of a polyisocyanate containing biuret groups, prepared from 1,6-diisocyanatohexane and having an NCO content (based on solution) of approximately 16.5%. The NCO/OH equivalent ratio was 1:1 in each case. Further details may be found in table IV below wherein the components are set forth in parts by weight.

After the addition of the curing agent, the polyacrylates were applied to a sheet of glass with a coating knife (210 μm). A thumb was firmly applied to the coated surface from time to time to test whether it was still tacky, whether any impression was left behind or whether no impression was visible on the film. The times set forth in Table IV represent the period of time after which the thumb left no impression.

Table IV

Lacquer	A	B	C	D	E	F	G
						Comparison coatings	
Polyacrylate from example 1	100	-	-	-	-	-	-
Polyacrylate from example 2	-	100	-	-	-	-	-
Polyacrylate from example 3	-	-	100	-	-	-	-
Polyacrylate from example 4	-	-	-	100	-	-	-
Polyacrylate from example 5	-	-	-	-	100	-	-
Polyacrylate from example 6	-	-	-	-	-	100	100
CAB 381-0.5*	-	-	-	-	-	-	15
Butyl acetate	72	51	140.5	182	164	70	328
Curing agent solution	12.1	12.6	13	13.6	12.5	14.9	22.6
Hand drying (in minutes)	48	54	55	44	56	>480	79

* A commercial cellulose acetate butyrate from Eastman Kodak.

As demonstrated in Table IV, comparison coating F had a hand drying time of over 8 hours. It is only after addition of cellulose acetate butyrate that the rapid hand drying time required in commercial use is achieved (comparison coating G). To the contrary, coatings A to E according to the invention exhibit the drying times required in commercial use even without cellulose acetate butyrate.

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:-

1. A binder composition for the production of rapidly physically drying coating compositions comprising

a) a polyisocyanate component having an NCO content of 10 to 30 wt.% and containing one or more organic polyisocyanates and

b) a hydroxy-functional polyacrylate component containing one or more hydroxy-functional polyacrylate resins having a number average molecular weight (M_n) of at least 10,000 and a viscosity as a 40 wt.% solution in n-butyl acetate at 23°C of at least 2,000 mPa.s,

wherein components a) and b) are present in amounts sufficient to provide an NCO/OH equivalent ratio of 0.5:1 to 2.0:1.

2. The binder composition of Claim 1 wherein component b) consists essentially of at least one hydroxy-functional polyacrylate resin produced by the copolymerization of

A) 2.5 to 30 wt.% of one or more hydroxyalkyl esters of acrylic and/or methacrylic acid,

B) 30 to 90 wt.% of methyl methacrylate,

C) 0 to 50 wt.% of styrene,

D) 0 to 2 wt.% of (meth)acrylic acid and

E) 0 to 50 wt.% of one or more C_1-C_{18} alkyl esters of acrylic and/or methacrylic acid other than those set forth in A) and B).

3. The binder composition of Claim 1 wherein component b) consists essentially of at least one hydroxy-functional polyacrylate resin produced by the copolymerization of

A) 2.5 to 20 wt.% of one or more hydroxyethyl (meth)acrylates, isomeric hydroxypropyl (meth)acrylates and/or hydroxybutyl (meth)acrylates,

B) 55 to 80 wt.% of methyl methacrylate,

C) 0 to 30 wt.% of styrene,

D) 0 to 2 wt.% of (meth)acrylic acid and

E) 0 to 30 wt.% of one or more C_1-C_8 alkyl (meth)acrylates other than those set forth in A) and B).

4. The binder composition of Claim 1 wherein component b) has an OH content, based on the solids, of 0.5 to 5 wt.%.

5. The binder composition of Claim 2 wherein component b) has an OH content, based on the solids, of 0.5 to 5 wt.%.

6. The binder composition of Claim 3 wherein component b) has an OH content, based on the solids, of 0.5 to 5 wt.%.

7. The binder composition of Claim 1 wherein component b) consists essentially of one or more polyacrylate resins produced by free-radical solution polymerization at 90-120°C using initiators with a half-life of 5-120 minutes.

8. A binder composition for the production of rapidly physically drying coating compositions comprising

a) a polyisocyanate component having an NCO content of 10 to 30 wt.% and containing one or more organic polyisocyanates containing biuret, urethane or isocyanurate groups and having an average NCO functionality of 2.5 to 6 and

b) a hydroxy-functional polyacrylate component containing one or more hydroxy-functional polyacrylate resins having a number average molecular weight (M_n) of at least 10,000 and a viscosity as a 40 wt.% solution in n-butyl acetate at 23°C of at least 2,000 mPa.s,

wherein components a) and b) are present in amounts sufficient to provide an NCO/OH equivalent ratio of 0.5:1 to 2.0:1.

9. The binder composition of Claim 8 wherein component b) consists essentially of at least one hydroxy-functional polyacrylate resin

produced by the copolymerization of

A) 2.5 to 30 wt.% of one or more hydroxyalkyl esters of acrylic and/or methacrylic acid,

B) 30 to 90 wt.% of methyl methacrylate,

C) 0 to 50 wt.% of styrene,

D) 0 to 2 wt.% of (meth)acrylic acid and

E) 0 to 50 wt.% of one or more C_1-C_{18} alkyl esters of acrylic and/or methacrylic acid other than those set forth in A) and B).

10. The binder composition of Claim 8 wherein component b) consists essentially of at least one hydroxy-functional polyacrylate resin produced by the copolymerization of

A) 2.5 to 20 wt.% of one or more hydroxyethyl (meth)acrylates, isomeric hydroxypropyl (meth)acrylates and/or hydroxybutyl (meth)acrylates,

B) 55 to 80 wt.% of methyl methacrylate,

C) 0 to 30 wt.% of styrene,

D) 0 to 2 wt.% of (meth)acrylic acid and

E) 0 to 30 wt.% of one or more C_1-C_8 alkyl (meth)acrylates other than those set forth in A) and B).

11. The binder composition of Claim 8 wherein component b) has an OH content, based on the solids, of 0.5 to 5 wt.%.

12. The binder composition of Claim 9 wherein component b) has an OH content, based on the solids, of 0.5 to 5 wt.%.

13. The binder composition of Claim 10 wherein component b) has an OH content, based on the solids, of 0.5 to 5 wt.%.

14. The binder composition of Claim 8 wherein component b) consists essentially of one or more polyacrylate resins produced by free-radical solution polymerization at 90-120°C using initiators with a half-life of 5-120 minutes.

15. A two-component polyurethane coating composition containing the binder composition of Claim 1 as the binder.